40677.1
PATENT **13426US**

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants:	Rohr *et al.*	Examiner:	To be assigned
Serial No.:	To be assigned	Group Art Unit:	To be assigned
Filed:	Herewith		
For:	*"Process for regenerating a nitrogen oxides storage catalyst"*		
Customer No.:	23719	Kalow & Springut LLP 488 Madison Avenue, 19th Floor New York, New York 10022	

July 29, 2003

Mail Stop Patent Application
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

TRANSMITTAL OF PRIORITY DOCUMENT

Sir:

Enclosed is a copy of the certified priority document for the above-identified application. If any fee is due please charge Deposit Account No. 11-0171 for such sum accordingly.

If there are any questions regarding this matter that need to be resolved, the Examiner is respectfully invited to contact the Applicants' attorney at the telephone number given below. Thank you for your time and attention to this matter.

Respectfully submitted,

Scott D. Locke, Esq.
Registration No.: 44,877
Attorney for Applicant

(212) 813-1600

Europäisches Patentamt

European Patent Office

Office européen des brevets

Bescheinigung

Certificate

Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. **Patent application No.** **Demande de brevet n°**

02017245.8

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk

Anmeldung Nr:
Application no.: 02017245.8
Demande no:

Anmeldetag:
Date of filing: 31.07.02
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

OMG AG & Co. KG
Rodenbacher Chaussee 4
63457 Hanau-Wolfgang
ALLEMAGNE

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se referer à la description.)

Process for regenerating a nitrogen oxides storage catalyst

In Anspruch genommene Prioriät(en) / Priority(ies) claimed /Priorité(s) revendiquée(s)
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/
Classification internationale des brevets:

B01J38/00

Am Anmeldetag benannte Vertragstaaten/Contracting states designated at date of filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR IE IT LI LU MC NL PT SE SK TR

31. Juli 2002

VOSSIUS & PARTNER
PATENTANWÄLTE
SIEBERTSTR. 4
81675 MÜNCHEN

EPO - Munich
80
31. Juli 2002

Process for regenerating a nitrogen oxides storage catalyst

FIELD OF THE INVENTION

The present inventions relates to cleaning of the exhaust gas of a diesel engine. In particular it deals with lowering the content of nitrogen oxides contained in the exhaust gas by using a nitrogen oxides storage catalyst. The process according to the invention provides a new strategy for regenerating the nitrogen oxides storage catalyst resulting in improved nitrogen oxides conversion at low exhaust gas temperatures.

BACKGROUND OF THE INVENTION

Diesel engines belong to the category of so-called lean-burn engines which are operated with lean air/fuel-ratios.

The air/fuel-ratio is calculated from the mass of air supplied to the engine in relation to the mass of fuel. Normal fuels for internal combustion engines such as diesel engines or gasoline engines require an air/fuel-ratio of approximately 14.6 for complete combustion, that is to say 14.6 kilograms of air are needed for the combustion of 1 kilogram of fuel. Air/fuel-ratios above that value are called lean and air/fuel ratios below said value are called rich. The exhaust gas leaving the engine exhibits the same air/fuel-ratio as the air/fuel-mixture supplied to the engine provided that no adsorption or desorption processes occur within the engine. Frequently the so-called λ-value is used to characterise the composition of the air/fuel-mixture or of the exhaust gas. The λ-value is equal to the air/fuel-ratio normalised to stoichiometric conditions. For stoichiometric combustion of the fuel the λ-value of the air/fuel mixture supplied to the engine must be equal to 1.

Diesel engines are operated with lean air/fuel-mixtures with λ-values above 1, usually with λ-values between 1.5 and 4. Therefore the exhaust gas of diesel engines contains a high concentration of oxygen between 5 and 15 vol.-% while stoichiometrically operated gasoline engines contain only around 0.7 vol.-% of oxygen.

Diesel engine exhaust gases contain harmful substances such as carbon monoxide (CO), unburnt hydrocarbons (HC), nitrogen oxides (NOx) and soot particles. The nitrogen oxides are a mixture of different oxides of nitrogen. The major component is nitrogen monoxide which amounts to 60 to 90 vol.-% of the total nitrogen oxides content of the exhaust gas, the balance being mainly nitrogen dioxide. The exact composition depends on the engine type and the current operating conditions.

Carbon monoxide and unburnt hydrocarbons can effectively be converted to harmless substances by contacting the exhaust gas with a diesel oxidation catalyst. But due to the high oxygen content of diesel exhaust gas it is difficult to convert the nitrogen oxides to harmless nitrogen gas. For coping with this problem nitrogen oxides storage catalysts have been developed which adsorb the nitrogen oxides during operating phases of the engine with lean exhaust gas and release nitrogen oxides and convert them to harmless substances during operating phases of the engine with rich exhaust gas.

A nitrogen oxides storage catalyst is composed mainly of a platinum catalyst and a storage component. The storage component comprises basic metal oxide compounds such as oxides of elements selected from the group consisting of alkali metals, alkaline earth metals, rare earth metals and mixtures thereof. The preferred storage components are barium oxide and strontium oxide. The well recognised theory about the functioning of such a catalyst is as follows:

During lean operating phases of the engine nitrogen monoxide contained in the exhaust gas is oxidised by the platinum catalyst to nitrogen dioxide which under the humid atmosphere of the exhaust gas gets trapped by the storage components in the form of nitrates. When the storage capacity of the storage components has been exhausted the nitrogen oxides storage catalyst has to be regenerated to restore its original storage capacity. For that aim the air/fuel-ratio of the air/fuel-mixture fed to the engine is changed to rich values. Under the reducing conditions established by the rich exhaust gas the adsorbed nitrogen oxides get desorbed and are converted by the platinum catalyst with the help of carbon monoxide and hydrocarbons contained in the rich exhaust gas to nitrogen, carbon dioxide and water.

Depending on the nominal storage capacity of the nitrogen oxides storage catalyst and the concentration of nitrogen oxides contained in the exhaust gas the time during which the nitrogen oxides storage catalyst can adsorb nitrogen oxides, the so-called storage phase, amounts to 1 to 5 minutes. Thereafter the catalyst has to be regenerated. Regeneration is done by lowering the λ-value of the exhaust gas to values between 0,9 and 0,95. Between 5 to 10 seconds of regeneration are needed to restore the storage capacity of the catalyst. Thus, storage and regeneration alternate frequently during operation of the engine.

By nature, diesel engines require strongly lean air fuel mixtures for stable operation. It was only with the development of new diesel engines (common rail engines and pump-injector engines) during the last years that it became possible to operate also diesel en-

gines with rich air/fuel-mixtures for a short period of time. This development made it possible to not only use nitrogen oxides storage catalyst for exhaust gas cleaning of lean operated gasoline engines but also for diesel engines.

Changing of the air/fuel ratio from lean to rich for regenerating the nitrogen oxides storage catalyst during driving must be performed in such a way that this change does not affect the driving comfort. Experience has shown that this condition restricts the maximum permissible regeneration time to approximately 8 to 20 seconds. But this time period is sufficient to completely regenerate the nitrogen oxides storage catalyst provided the exhaust gas temperature is high enough.

As already indicated, the above described mechanism is strongly dependent on the exhaust gas temperature and the temperature of the nitrogen oxides storage catalyst. Above a certain threshold temperature which amounts to approximately 170 to 250 °C the described mechanism functions well. But below this temperature range regeneration becomes difficult.

The newly developed diesel engines exhibit relatively low average exhaust gas temperatures. This causes problems when regenerating the nitrogen oxides storage components especially after prolonged storage periods. The conventional regeneration procedure involves brief rich periods during which the stored nitrogen oxides are released and subsequently converted to nitrogen (N_2). However, at low temperatures a substantial amount of the nitrogen oxides being released leave the converter unreduced probably due to slow kinetics of the chemical reactions involved in the conversion of nitrogen oxides. Furthermore, the storage components are only partly cleared, that is, some nitrates remain in the storage material, hence lowering the storage capacity for the next storage cycle. The situation is aggravated even further since hydrocarbon and carbon monoxide breakthroughs during the rich phase are also common under these conditions. Once again, slow kinetics at the given temperatures may be the reason. Heating measures in lean atmosphere by post injection have been proved to be quite ineffective in improving the performance of nitrogen oxides storage catalysts since the temperature increase achieved by these methods drop very quickly after switching back to normal operation mode.

Therefore there is the need in the art for improving the regeneration of nitrogen oxides storage catalysts especially at low exhaust gas and catalyst temperatures.

SUMMARY OF THE INVENTION

According to the invention two regeneration strategies for regenerating the nitrogen oxides storage catalyst are provided. A first regeneration strategy is applied when the exhaust gas temperature of the diesel engine is above a threshold value and a second strategy is applied when the exhaust gas temperature is below said threshold value. The threshold value is dependent on the formulation of the catalyst and its ageing status. Usually this value lies between 170 and 250 °C.

The first strategy is identical to the conventional regeneration of nitrogen oxides traps. For that purpose the air/fuel ratio is changed from lean to rich during a regeneration period and the adsorbed nitrogen oxides are desorbed and converted to nitrogen.

The second regeneration strategy comprises switching the air/fuel-ratio between said rich and said lean air-fuel-ratio back and force forming a sequence of rich lean/pulses with a number of 2 to 10 rich/lean pulses.

The second regeneration strategy improves the overall performance of the exhaust gas cleaning process considerably. At temperatures below the threshold value the conventional regeneration strategy is unable to fully restore the original storage capacity of the catalyst and leads to strong emissions of carbon monoxide and hydrocarbons during the regeneration period. When the nitrogen oxides storage catalyst is operated over a prolonged period at low exhaust gas temperatures regeneration gets worse. After each regeneration the residual nitrogen oxides remaining on the catalyst increases.

It has been observed that in some instances the first regeneration strategy can be omitted. In that case the pulsed regeneration strategy is used under all operation conditions of the diesel engine even when the exhaust gas temperature is high.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a process for regeneration of a nitrogen oxides storage catalyst arranged in the exhaust gas system of a diesel engine wherein the exhaust gas has an exhaust gas temperature and an air/fuel-ratio. Said process comprises a first and a second regeneration strategy wherein the first regeneration strategy is applied when the exhaust gas temperature is above a threshold value and comprises changing the air/fuel ratio from a lean to a rich value during a first regeneration period and wherein the second regeneration strategy is applied when the exhaust gas temperature is below said

threshold value and comprises switching the air/fuel-ratio between said lean and said rich air/fuel-ratio back and force forming a sequence of rich/lean-pulses with a number of 2 to 10 rich/lean pulses during a second regeneration period.

The conventional procedure for the regeneration of a nitrogen oxides storage catalyst involves running the catalyst in rich atmosphere for some seconds (typically 5 to 20 s). The engine management continuously monitors the state of the storage catalyst. If the storage performance of the catalyst drops below a critical value, regeneration is initiated. The engine switches from lean conditions with λ in the range between1.5 and 4 to a rich operation point with λ in the range from 0.98 to 0.8 without change of torque so that the driver does not recognises the start of regeneration. As mentioned above, this procedure yields poor results at low exhaust gas temperatures below a certain threshold temperature. This threshold temperature lies between 170 and 250 °C depending on the catalyst used and its ageing state.

A substantially improved removal of the nitrous species from the catalyst combined with highly efficient conversion to nitrogen at low exhaust gas temperatures is achieved by means of a pulsed regeneration procedure. The catalyst is regenerated using a sequence of rich/lean-pulses. The engine management switches the air/fuel-ratio supplied to the engine back and forth between the normal lean operating point and a corresponding torque-neutral rich operating point. The lambda values are the same as for the conventional regeneration procedure.

The duration of the pulses (their pulse width) is in the order of 2 to 10 seconds and may be the same or different for the rich and the lean pulses. The ratio of the pulse width of the lean pulses to the pulse width of the rich pulses may lie between 5:1 and 1:5. Moreover the pulse widths of the pulses may be decreased stepwise or continuously from the beginning to the end of said second regeneration period.

During the pulsed regeneration a progressive increase of the catalyst temperature is observed which facilitates carbon monoxide and hydrocarbon conversion as well as the release and reduction of the nitrous oxides. A number of 2 to 10 rich/lean-pulses have proved sufficient for complete regeneration of the catalyst.

In fact, it seems that the key factor of the pulsed regeneration is the combination of heating and regeneration. By switching between lean and rich, a steady oxygen supply is maintained that helps to burn the hydrocarbons being deposited on the catalyst during

the rich pulses. The increased temperature then speeds up the relevant chemical reactions.

Conventional regeneration is done for a regeneration period of approximately 5 to 20 seconds. This period cannot be prolonged considerably in order to improve regeneration without loosing stability of engine operation and driving comfort. Contrary to that it was found that the pulsed regeneration allows longer regeneration periods without the detrimental effects observed during conventional regeneration.

Having now generally described the invention, the same may be more readily understood through reference to the following figures and examples, which are provided by way of illustration and are not intended to limit the present invention unless specified.

Figure 1: Shows operation of a nitrogen oxides storage catalyst arranged in the exhaust gas system of a diesel engine using the novel pulsed regeneration strategy according to the invention at low exhaust gas temperatures.

Figure 2: Shows operation of a nitrogen oxides storage catalyst arranged in the exhaust gas system of a diesel engine using the conventional regeneration strategy at low exhaust gas temperatures.

EXAMPLES

Example 1:

The novel pulsed regeneration strategy was applied during the operation of a nitrogen oxides storage catalyst arranged in the exhaust system of a diesel engine.

The diesel engine was a common rail engine and had a power rating of 90 kW and a displacement volume of 2.2 l. The nitrogen oxides storage catalyst consisted of a honeycomb carrier with the catalyst deposited thereon in the form of a coating. The honeycomb carrier had a diameter of 14.38 cm (5.66 inch) and a length of 15.24 cm (6 inch) with a total volume of 2.47 l. The cell density of this carrier was 62 cm^{-2} (400 $inch^{-2}$).

The storage catalyst had been applied to this catalyst carrier with a concentration of 280 g per liter of honeycomb carrier. The storage component was barium oxide. The storage catalyst further contained platinum and rhodium in a weight ratio of 10:1 and a combined concentration of 3.88 g/l (110 g/ft^3).

Figure 1 shows measurement scans of various quantities of the exhaust gas and of the catalyst over an operation period of the diesel engine of 1000 seconds. The following quantities were measured online:

- Lambda value before the catalyst (Lambda,in); measured with a lambda sensor
- Nitrogen oxides concentrations in the exhaust gas before (NOx,in) and after the catalyst (NOx,out); measured with a chemo-luminescence detector
- Catalyst temperature measured at entrance of catalyst (T1)
- Catalyst temperature midway of the catalyst (T2)
- Catalyst temperature measured at exit of catalyst (T3).

During the test the engine was operate at a constant rotation speed of 1500 rpm without exhaust gas recirculation. This resulted in a space velocity of the exhaust gas relative to the catalyst of 30,000 h^{-1}. At the start of the test the catalyst was conditioned by operating the diesel engine with 5 rich/lean pulses with a duty cycle of 20/10. The amplitudes of the pulses were switched between 3.3 and 0.9. After that the engine was operated for 200 seconds with a lambda value of approximately 3.3 (storage phase). During this phase nitrogen oxides were stored on the storage catalyst. At the end of this storage phase the catalyst temperature had dropped below 250 °C.

During the storage phase the concentration of nitrogen oxides in the exhaust gas before the catalyst (NOx,in) was approximately 330 ppm. At the beginning of the storage phase no nitrogen oxides were leaving the catalyst (NOx,out) which demonstrates that all nitrogen oxides contained in the exhaust gas were trapped on the storage catalyst. But soon a leakage of nitrogen oxides could be observed which amounted to 180 ppm at the end of the storage phase. Then a pulsed regeneration was initiated comprising 5 rich/lean pulses. After regeneration the nitrogen oxides concentration at the outlet of the catalyst was again zero, indicating complete regeneration of the catalyst. Storage phase and regeneration phase were repeated several times.

From the lower diagram in Figure 1 it can be seen that the pulsed regeneration led to a temperature increase of the catalyst of up to 350 °C.

Comparison Example 1:

The same test procedure was repeated with conventional regeneration. The regeneration period was set to 8 seconds which was the maximum allowable period with rich air/fuel-ratio for this engine. The respective measurement scans can be seen in Figure 2.

From the upper diagram in Figure 2 it can be seen that from regeneration period to regeneration period the storage catalyst gets less regenerated so that the catalyst adsorbs less nitrogen oxides from the exhaust gas resulting in an increasingly enhanced concentration of nitrogen oxides at the outlet of the catalyst.

While the invention has been described in connection with specific embodiments thereof, it will be understood that it is capable of further modifications and this application is intended to cover any variation, uses, or adaptations of the invention following, in general, the principles of the invention and including such departures from the present disclosure as come within known or customary practice within the art to which the invention pertains and as may be applied to the essential features hereinbefore set forth and as follows in the scope of the appended claims.

CLAIMS

1. Process for regeneration of a nitrogen oxides storage catalyst arranged in the exhaust gas system of a diesel engine wherein the exhaust gas has an exhaust gas temperature and an air/fuel-ratio, said process comprising a first and a second regeneration strategy wherein the first regeneration strategy is applied when the exhaust gas temperature is above a threshold value and comprises changing the air/fuel ratio from a lean to a rich value during a first regeneration period and wherein the second regeneration strategy is applied when the exhaust gas temperature is below said threshold value and comprises switching the air/fuel-ratio between said lean and said rich air/fuel-ratio back and force forming a sequence of rich/lean-pulses with a number of 2 to 10 rich/lean pulses during a second regeneration period.

2. Process according to claim 1, wherein the threshold temperature is selected from the interval between 170 and 250 °C.

3. Process according to claim 2, wherein said lean air/fuel-ratio lies between 1.5 and 4 and said rich air/fuel-ratio lies between 0.8 and 0.98.

4. Process according to claim 3, wherein the duration of the first regeneration period is of from 5 to 20 seconds.

5. Process according to claim 4, wherein the pulse width of the lean and the rich pulses are the same or different and lie between 2 and 10 seconds.

6. Process according to claim 5, wherein the ratio of the pulse width of the lean pulses to the pulse width of the rich pulses lies between 5:1 and 1:5.

7. Process according to claim 6, wherein the pulse widths of the pulses is decreased stepwise or continuously from the beginning to the end of said second regeneration period.

8. Process for regeneration of a nitrogen oxides storage catalyst arranged in the exhaust gas system of a diesel engine wherein the exhaust gas of the diesel engine has an exhaust gas temperature and an air/fuel-ratio, and wherein the nitrogen oxides contained in the exhaust gas are adsorbed by the storage catalyst during normal operating conditions of the engine with a lean air/fuel-ratio and the nitrogen oxides are desorbed and converted to harmless substances by lowering the

air/fuel-ratio to a rich value during a regeneration period, wherein during the regeneration period the air/fuel-ratio is switched back and force between said lean and said rich air/fuel-ratio forming a sequence of rich/lean-pulses with a number of 2 to 10 rich/lean pulses.

9. Process according to claim 8, wherein said lean air/fuel-ratio lies between 1.5 and 4 and said rich air/fuel-ratio lies between 0.8 and 0.98.

10. Process according to claim 9, wherein the pulse widths of the lean and the rich pulses are the same or different and lie between 2 and 10 seconds.

11. Process according to claim 10, wherein the ratio of the pulse width of the lean pulses to the pulse width of the rich pulses lies between 5:1 and 1:5.

12. Process according to claim 11, wherein the pulse widths of the pulses is decreased stepwise or continuously from the beginning to the end of said regeneration period.

13. Device for regeneration of a nitrogen oxides storage catalyst arranged in the exhaust gas system of a diesel engine wherein the exhaust gas has an exhaust gas temperature and an air/fuel-ratio, the device being particularly adapted to carry out a process according to any one of the preceding claims, said device comprising:

means for providing/generating a first and a second regeneration strategy,

wherein the first regeneration strategy is applicable when the exhaust gas temperature is above a threshold value and comprises changing the air/fuel ratio from a lean to a rich value during a first regeneration period and

wherein the second regeneration strategy is applicable when the exhaust gas temperature is below said threshold value and

means for switching the air/fuel-ratio between said lean and said rich air/fuel-ratio back and force forming a sequence of rich/lean-pulses with a number of 2 to 10 rich/lean pulses during a second regeneration period.

ABSTRACT

The present invention provides a process and a device for regeneration of a nitrogen oxides storage catalyst arranged in the exhaust system of a diesel engine. The process comprises a first and a second regeneration strategy wherein the first regeneration strategy is applied when the exhaust gas temperature is above a threshold value and comprises changing the air/fuel ratio from a lean to a rich value during a first regeneration period and wherein the second regeneration strategy is applied when the exhaust gas temperature is below said threshold value and comprises switching the air/fuel-ratio between said lean and said rich air/fuel-ratio back and force forming a sequence of rich/lean-pulses with a number of 2 to 10 rich/lean pulses during a second regeneration period.

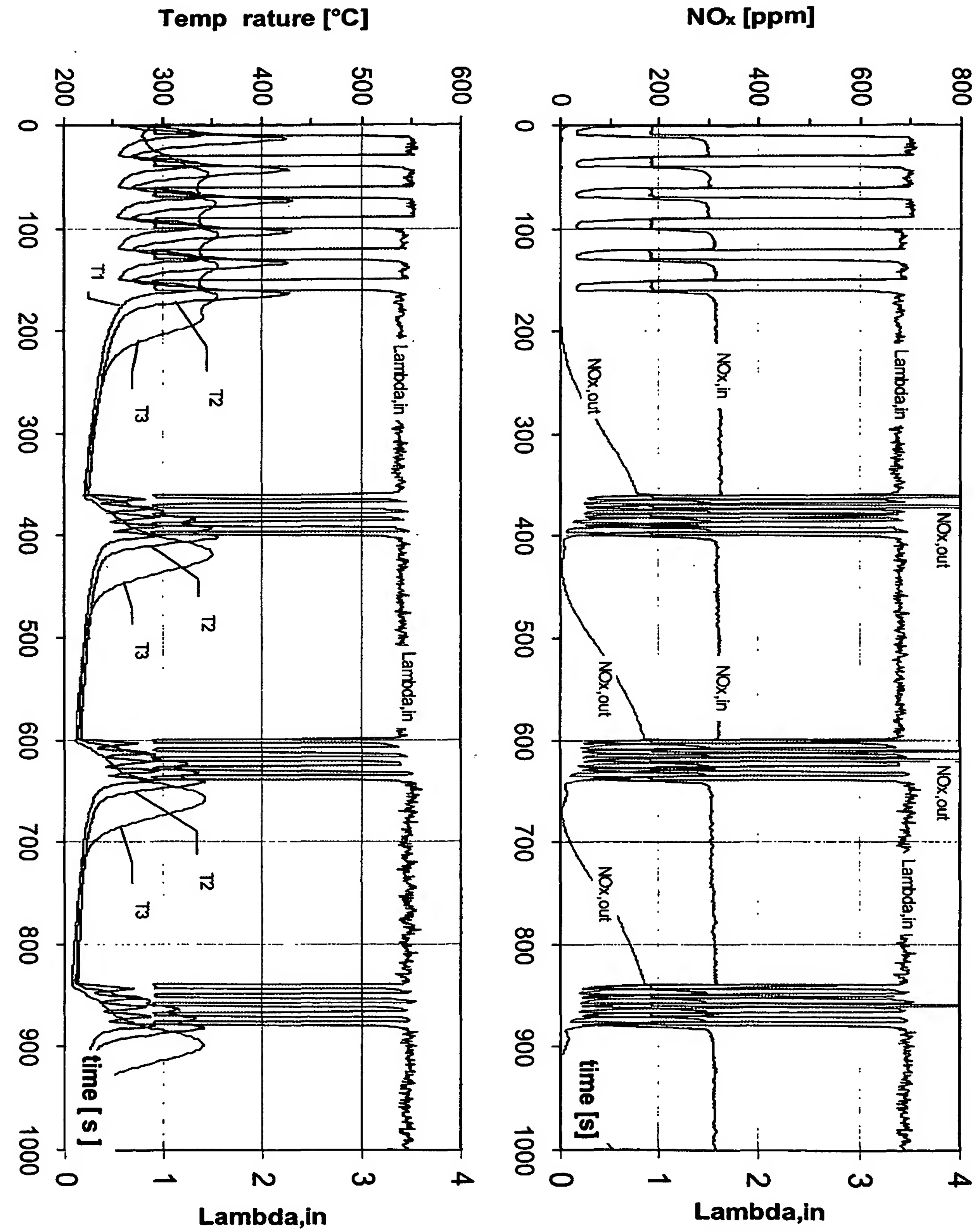
NOx [ppm]
Temp rature [°C]
Lambda,in
Lambda,in
NOx,in
NOx,out
Lambda,in
T1
T2
T3
time [s]
time [s]
0
100
200
300
400
500
600
700
800
900
1000
0
1
2
3
4
0
200
400
600
800
200
300
400
500
600

Fig. 1

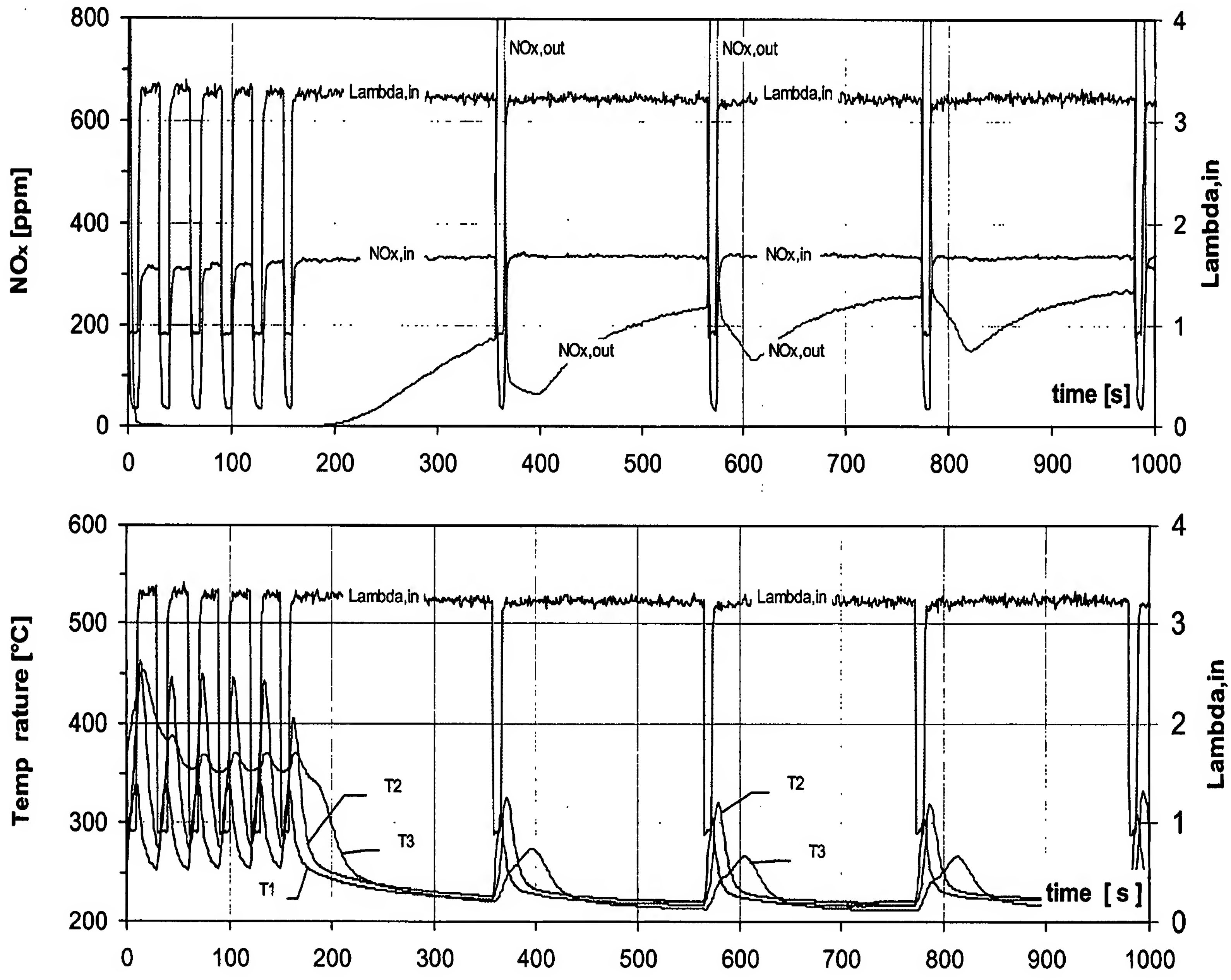
NOx [ppm]
Lambda,in
NOx,in
NOx,out
time [s]
Temp rature [°C]
T1
T2
T3
time [s]
0
100
200
300
400
500
600
700
800
900
1000

Fig. 2